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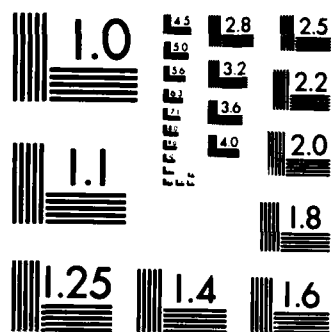
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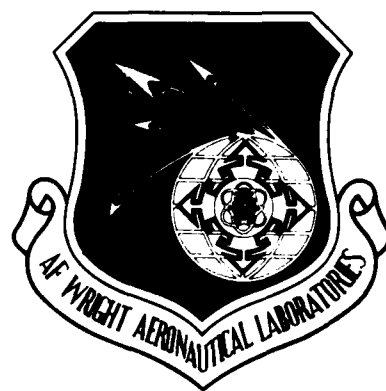
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# AD-A157 340

STUDIES ON CHALCOGENIDE FILMS



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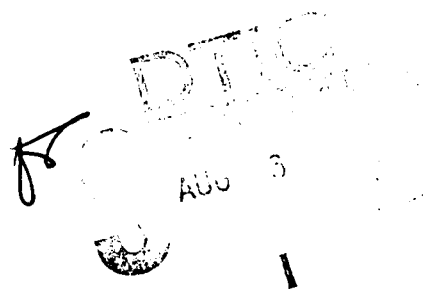
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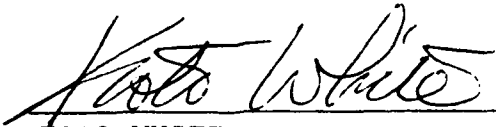
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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

  
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			glass transition temperature and structural relaxation.		

## PREFACE

This report summarizes research performed at the Materials Laboratory, Wright-Patterson Air Force Base, from February 1, 1984 to January 31, 1985 under UES Contract No. F33615-82-C-5001/SB 5448-82-C-0076, Project #729.

The author would like to acknowledge the support of Mr. Conrad M. Phillippi for providing specimens, fruitful discussions and experimental help throughout the duration of the project.

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# TABLE OF CONTENTS

SECTION		PAGE
I	INTRODUCTION	1
II	THERMAL SENSITIVITY OF REFLECTION FILTERS	2
	1. BACKGROUND	2
	2. $dn/dT$ OF MATERIALS	3
	3. EFFECT OF IMPERFECTIONS	7
	4. CHARACTERIZATION TECHNIQUE	9
III	THERMAL AGING EFFECTS IN VITREOUS $As_2S_3$ FILMS	10
	1. INTRODUCTION	10
	2. EXPERIMENTAL	10
	3. RESULTS	11
IV	STOICHIOMETRY OF $As_2S_3$ FILMS	19
	1. INTRODUCTION	19
	2. RESULTS	19
V	SUMMARY AND CONCLUSIONS	24
	REFERENCES	26

# LIST OF ILLUSTRATIONS

FIGURE NO.		PAGE
1	$dn/dT$ Range for Various Glass Systems.	6
2	Temperature Coefficient of Refractive Index of Materials -- A Schematic Representation.	8
3	A Typical Transmitted Interference Fringe Pattern Versus Wave Number.	12
4	Refractive Index with Annealing Time.	14
5	Property as a Function of Temperature for Vitreous Materials.	16
6	Schematic Representation of Compaction During Aging.	18
7	Typical As and S Peaks Observed in EDXA.	20
8	Plot of R as a Function of Film Deposition Rate.	23



## LIST OF TABLES

TABLE NO.		PAGE
1	Properties of Some Chalcogenide Glasses.	3
2	EDXA Analysis of Film and Substrate Composition.	21

## SECTION I

### INTRODUCTION

This program was initiated with an objective to develop an understanding of the thermal sensitivity parameter of chalcogenide narrow band reflection filters. Specifically, two areas were identified for study:

1. To conduct a literature review and compile information on the effects of composition on thermal expansion ( $\alpha$ ), refractive index ( $n$ ), and temperature coefficient of refractive index ( $dn/dt$ ) among chalcogenide glass forming systems.

2. To correlate composition and properties so that a prediction could be made to achieve zero or near-zero thermal sensitivity parameter ( $1/n \partial n/dT + \alpha$ ).

There are two different types of thermal sensitivity of chalcogenide glasses that are of interest to us. The first one is of reversible type. In this case as the temperature varies, the optical properties follow the temperature variation. After the filter is brought to the original temperature, the physical properties also assume the original values. The second type is of irreversible nature. In this case, the physical properties do not follow the temperature variation. Both of these situations have been considered and analyzed in view of the available information. Sections II and III of this report evaluate the reversible and irreversible changes respectively. Section IV reports and discusses the effect of deposition rate on the stoichiometry of  $As_2S_3$  films.

SECTION II  
THERMAL SENSITIVITY OF REFLECTION FILTERS

1. BACKGROUND

Optical thin films and related devices are likely to be exposed to a hostile and variable environment. A temperature fluctuation is an example of the variable environment and thin films exposed to such an environment may exhibit a substantial degradation (reversible and irreversible) in the designed performance. To minimize this problem, materials properties must be optimized. A relatively small variation in temperature and its effect on the performance of a narrow band pass reflection filter is considered and analyzed in the next few paragraphs.

The reflection peak ( $\lambda_0$ ) from an alternating layer of dielectric stack is given by

$$\lambda_0 = 4n_H d_H = 4n_L d_L \quad (1)$$

where  $n$  = refractive index,  $d$  = thickness, and  $H$  and  $L$  = high and low refractive index layers. By differentiating Equation 1 with respect to temperature one obtains

$$\frac{1}{\lambda_0} \frac{d\lambda_0}{dT} = \frac{1}{n} \frac{dn}{dT} + \alpha \quad (2)$$

The shift in the reflection peak due to a given temperature variation depends upon three parameters, i.e.  $n$ ,  $dn/dT$ , and  $\alpha$ . These three parameters and  $1/\lambda_0 \cdot d\lambda_0/dT$  for some chalcogenide glasses are presented in Table 1. For the sake of illustration, let us assume some values to determine the magnitude of shift in the reflection peak due to a given temperature fluctuation. Let  $\Delta T = 100^\circ\text{C}$ ,  $\lambda_0 = 10.6 \mu\text{m}$  ( $\text{CO}_2$  laser) and  $1/\lambda \Delta\lambda_0/T = 20 \times 10^{-6}/^\circ\text{C}$ . Using these parameters one obtains a value of  $\Delta\lambda = .0212 \mu\text{m}$  or  $212\text{\AA}$ . This shift in the reflection peak appears to be significant.

**TABLE 1**  
**PROPERTIES OF SOME CHALCOGENIDE GLASSES**

	$n$	$\frac{dn}{dT}(\times 10^6)$	$\alpha(\times 10^6)$	$\frac{1}{\lambda_o} \frac{d\lambda_o}{dT} = \frac{1}{n} \frac{dn}{dT} + \alpha$
$As_2S_3$	2.41	- 8.6	25	$21.46 \times 10^{-6}$
$Si_{25}As_{25}Te_{50}$	2.93	20.0	13	$19.83 \times 10^{-6}$
$Ge_{28}Sb_{12}Se_{60}$	2.60	79.0	16	$46.38 \times 10^{-6}$
(TI 1173)				

It should be noted from Table 1 that a significant change in  $1/\lambda_o \times d\lambda_o/dT$  seems to be achievable by compositional variation. Ideally, an equal but opposite value of  $1/n \, dn/dT$  and  $\alpha$  would be preferable. Many materials are known to have a negative temperature coefficient of refractive index ( $dn/dT$ ) but only a few materials exhibit a negative coefficient of thermal expansion. Thus, in order to minimize the  $1/\lambda_o \cdot d\lambda_o/dT$  parameter, development of a negative  $dn/dT$  material would be desirable.

## 2. $dn/dT$ OF MATERIALS

Although temperature coefficient of refractive index ( $dn/dT$ ) is an important property of optical materials, there is a lack of scientific understanding in regard to the effects of various parameters. It is logical to speculate that the bulk composition would have a significant effect on  $dn/dT$ . However, this simplistic view may not be entirely correct as we will see that the  $dn/dT$  is a complex property and one needs to be careful speculating or predicting  $dn/dT$  of a given optical material.

There are two types of materials that are of interest to us, i.e. dielectric and semiconductor types. These two materials respond differently to electromagnetic radiation and thus they must be treated separately. In addition, there are materials which fall between the broad classifications, i.e. dielectrics and semiconductors. These materials should be characterized accordingly.

a. Dielectrics -- A mathematical expression relating  $dn/dT$ , refractive index, and polarizability for glasses has been derived by L. Prod'homme (Reference 1). He applied the concept of refractive invariant; originally used for gases and later used for liquids and isotropic solids by Lorentz-Lorenz. The Lorentz-Lorenz equation is expressed by Equation 3.

$$\frac{n^2-1}{n^2+2} V = R \quad (3)$$

where  $n$  = refractive index,  $V$  = specific or molar volume, and  $R$  = specific or molar refractivity.

Rearranging and differentiating Equation 3 with respect to temperature one obtains:

$$\frac{\partial n}{\partial T} = \frac{(n^2-1)(n^2+2)}{6n} \left( \frac{1}{R} \cdot \frac{\partial R}{\partial T} - \frac{1}{V} \cdot \frac{\partial V}{\partial T} \right) \quad (4)$$

The terms  $1/R \cdot \partial R / \partial T$  and  $1/V \cdot \partial V / \partial T$  represent the electronic polarizability ( $\emptyset$ ) and volume expansion coefficient ( $\beta$ ), respectively. The Equation 4 can be further expressed by:

$$\frac{\partial n}{\partial T} = \frac{(n^2-1)(n^2+2)}{6n} (\emptyset - \beta) \quad (5)$$

Equation 5 should be examined in view of three possible situations:

(a)  $\emptyset > \beta$ : Most of the silicate and borosilicate glasses fall into this category because of their low thermal expansion

coefficient. In this case, polarization phenomenon dominates and  $\partial n/\partial T$  has a positive value.

(b)  $\alpha \approx \beta$ : This condition must be satisfied for zero or near zero  $\partial n/\partial T$  materials. High expansion glasses such as phosphate, fluorophosphate, and halide glasses fall into this category.

(c)  $\alpha < \beta$ : Many organic glasses, some phosphate glasses, and alkali halides (CsBr, CsI) satisfy this condition. Materials from this category exhibit large but negative  $\partial n/\partial T$ . We have compiled  $\partial n/\partial T$  data for various oxide glass systems which are shown in Figure 1. Interestingly, there is a wide range of  $\partial n/\partial T$  values for various glass systems.

b. Semiconductors -- For semiconductors, an empirical expression known as Moss's formula can be used to derive expression for  $dn/dT$ , i.e.

$$n^4 E_g = \kappa \quad (6)$$

where  $E_g$  = band gap and  $\kappa$  = constant. Differentiating Equation 6 one obtains

$$\frac{\partial n}{\partial T} = - \frac{n}{4E_g} \frac{\partial E_g}{\partial T} \quad (7)$$

Rabindra (Reference 2) has proposed another formula as expressed by Equation 8 for  $dn/dT$  of semiconductors

$$\frac{dn}{dT} = -0.62 \frac{dE_g}{dT} \quad (8)$$

The two expressions, i.e. Equations 7 and 8 clearly show the importance of temperature derivative of band gap on  $dn/dT$ . As most of the semiconductors have a negative  $dE_g/dT$ , it is expected that these semiconductors would exhibit a positive  $dn/dT$ . The band gap and its temperature derivative of well-known semiconductors (Si, Ge, GaP, etc.) are fairly well characterized.

SECTION IV  
STOICHIOMETRY OF  $\text{As}_2\text{S}_3$  FILMS

1. INTRODUCTION

$\text{As}_2\text{S}_3$  is an important optical material as it provides a wide spectral transparency in the infrared region. It is also well suited for making thin films and related optical devices utilizing the physical vapor deposition process (PVD). During the PVD process,  $\text{As}_2\text{S}_3$  is evaporated and possibly decomposed before deposition on a suitable substrate. Several different chemical species could conceivably be formed during the evaporation process. The stoichiometry of the film resulting from varied condensation and deposition rates of these chemical species would be expected to be different from those of the starting  $\text{As}_2\text{S}_3$  material. Based on this consideration, four  $\text{As}_2\text{S}_3$  films on the  $\text{As}_2\text{S}_3$  substrate, having the film deposition rates of 15, 100, 210, and  $310 \text{ \AA sec}^{-1}$ , were characterized by SEM and Energy Dispersive X-ray Analysis (EDXA). The results are presented in the following paragraphs.

2. RESULTS

Figure 7 shows typical As and S peaks observed for the  $\text{As}_2\text{S}_3$  material. Table 2 presents As and S intensities expressed in counts per unit time from the three films and substrates. Three other parameters,  $S'$ ,  $S''$ , and  $R$  which characterize the chemistry of the film are also presented in the table. The  $S'$  represents  $S/\text{As}$  ratio, whereas  $S''$  represents  $S/(S+\text{As})$  ratio. In order to obtain a number which could characterize each coating rate irrespective of the substrate, the parameter  $R$  was developed and has been defined as  $S_f''/S_s''$ , where subscripts  $f$  and  $s$  represent the

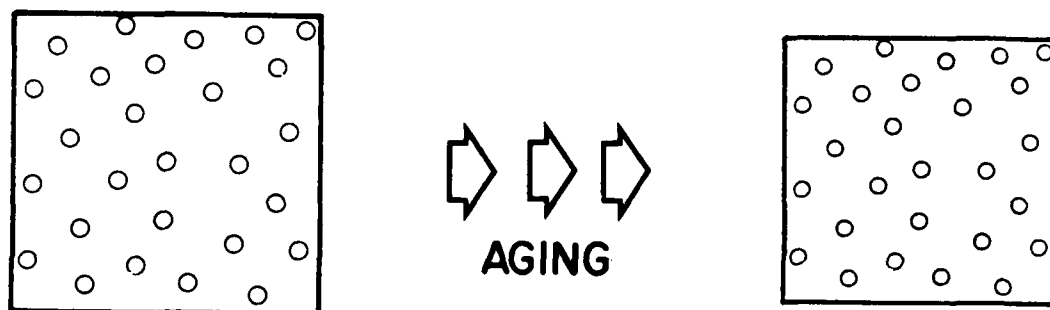


Figure 6. Schematic representation of compaction during aging.



or discontinuous transition between the vapor and condensed phase is expected. These two proposed features for a condensed vitreous solid obtained from a vapor phase are included in Figure 5.

The aging of the  $\text{As}_2\text{S}_3$  films and their effects on the properties are basically governed by the concepts presented in the previous two paragraphs. A thin film prepared by the PVD process will tend to stabilize its structure with time, and eventually will resemble the structure of a slowly cooled or annealed material. The time scale of structural stabilization depends upon the aging temperature. The time scale is shortened as the aging temperature approaches the glass transition temperature. The data presented in Figure 4 are consistent with the proposed mechanism of the structural stabilization.

During the aging process, any change in the stoichiometry or a major change in the nature of chemical bonding is unlikely. The increased refractive index as a function of aging time and temperature results from a structural compaction as illustrated in Figure 6. It is conceivable that the interatomic distance would decrease and densification will occur during aging process. This densification would result in an increase in the refractive index. Similar observations for  $\text{As}_2\text{S}_3$  films that were heat treated between  $T_g$  and room temperature have been reported by Xue-Xian et al. (Reference 9).

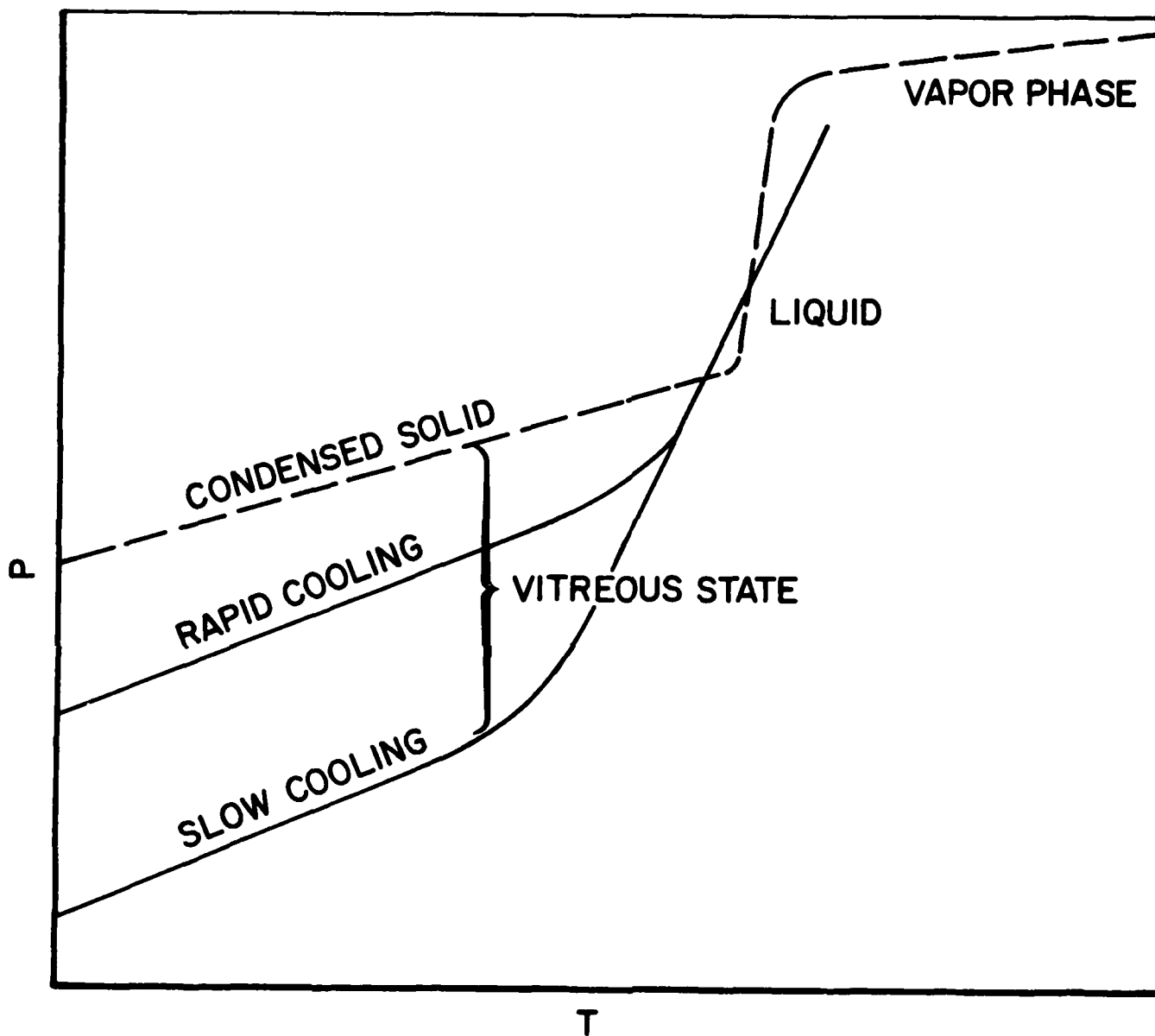


Figure 5. Property as a function of temperature for vitreous materials.

It is interesting to note from Figure 4 that the increase in refractive index due to the aging effect amounts to about 4%. This is a relatively large change as compared to the variation in refractive index due to annealing in other vitreous materials such as an oxide glass. For a bulk borosilicate crown glass, the refractive index change due to annealing is reported to be approximately 0.6% (Reference 7).

The structural evolution or relaxation of a vitreous material either prepared from a melt or a vapor phase is conveniently expressed (Reference 8) by a diagram as shown in Figure 5. A glass forming liquid cooled from a high temperature to room temperature shows two distinct linear regions of properties such as specific volume ( $\text{cm}^3/\text{gm}$ ). The regions intersect at a temperature known as the glass-transition temperature. The nonlinear region of the curve, both below and above the glass transition temperature represents the glass transformation range. In this range the structure is strongly influenced by the thermal history. For example, the rate of cooling through this range has a significant effect on the structure and resulting properties of a vitreous material. A rapid and slow cooling rate will result in a larger specific volume or a lower specific volume, respectively, as illustrated in the figure.

In general, a vitreous material prepared from the vapor phase exhibits structure similar to the one prepared from the liquid state. It is conceivable that the condensed vitreous solid would exhibit even more open and disorganized structure than those prepared by a rapidly cooled liquid. In addition, an abrupt

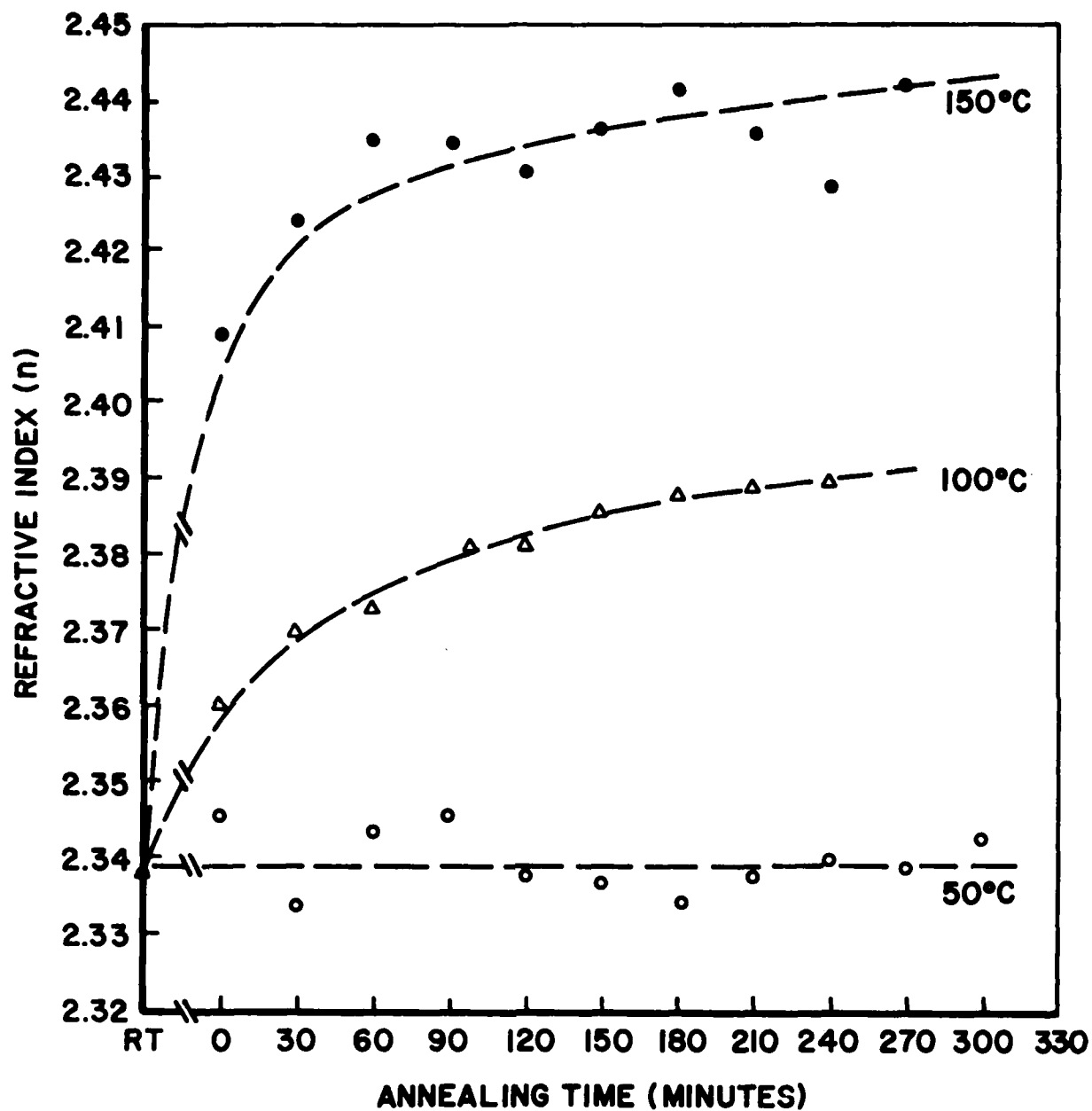


Figure 4. Refractive index with annealing time.

satisfied by Eqs. (9) and (10), respectively (Reference 6) where

$$n_2 \gtrsim n_1 \gtrsim n_0$$

$$n_1 d_1 = (2m+1)\lambda/4 \quad (9)$$

$$n_1 d_1 = (2m+2)\lambda/4 \quad (10)$$

where  $n_1$  = refractive index of film,  $n_0$  = refractive index of air,  $d_1$  = film thickness,  $m$  = an integer, and  $\lambda$  = wavelength. A plot of the order of fringe vs  $1/\lambda$  gives a straight line and the slope of the line is equal to two times the optical thickness ( $nd$ ). This optical thickness divided by the physical thickness as measured by Dektak IIa yields the refractive index. One of the limitations of this technique is that the specimen must be removed from the aging chamber and cooled down to room temperature before the thickness could be measured. The technique, however, allows one to determine the thickness before and after the aging and for intermediate conditions the thickness is obtained by interpolation. A typical thickness change due to aging was approximately 2%.

Figure 4 shows a plot of refractive index versus aging time at three temperatures (50°C, 100°C, and 150°C) for an  $\text{As}_2\text{S}_3$  film deposited on the Servofrax<sup>®</sup> substrate. At 50°C, the aging time has little effect on the refractive index. There is a substantial increase in the refractive index as the aging temperatures are increased to 100°C and 150°C. At these temperatures, a rapid change in the refractive index in the earlier stages of aging is followed by a slower change at later stages - a typical relaxation behavior. As one can expect, the rate of relaxation increases as the heat treatment temperature approaches the glass transition temperature.

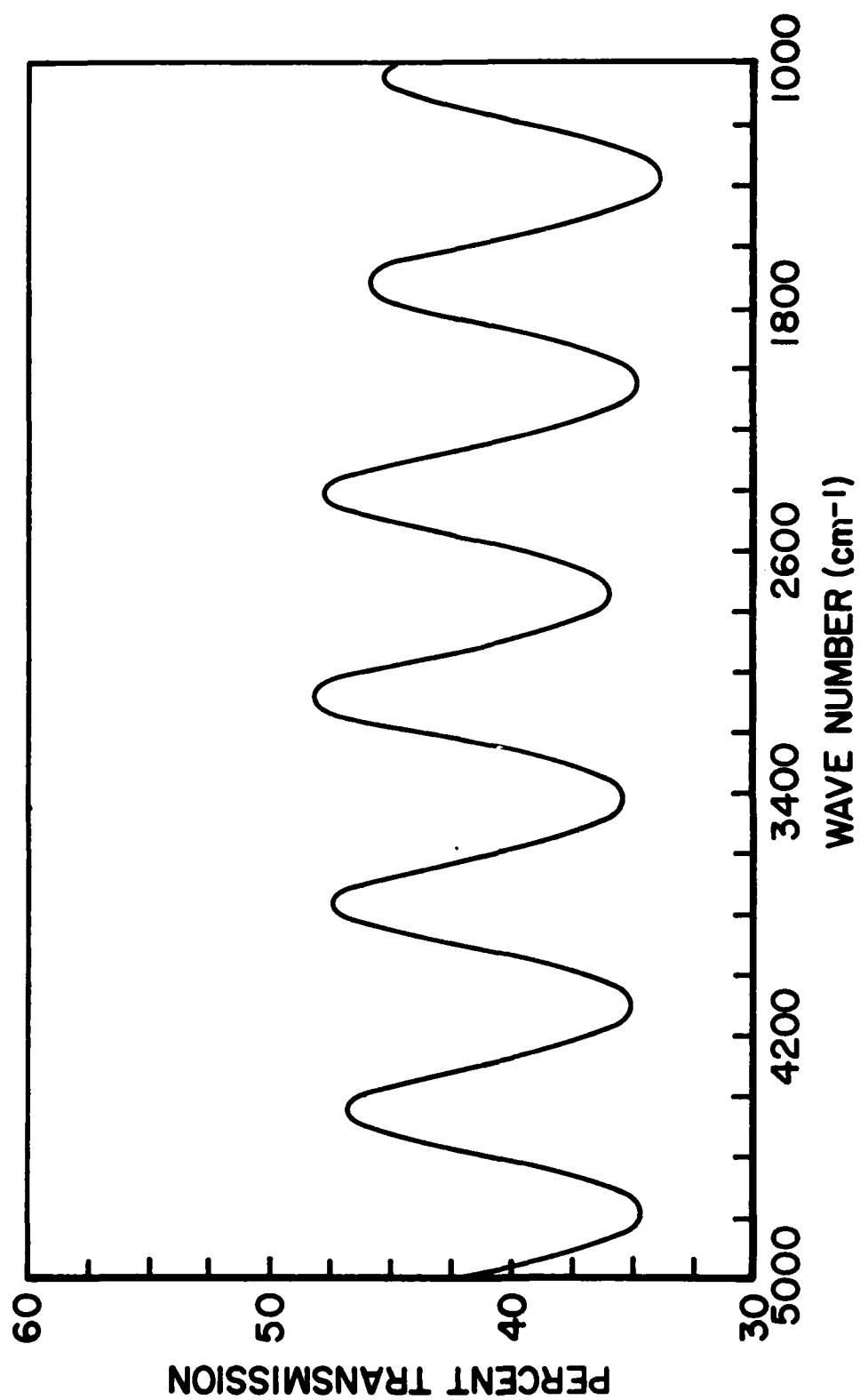


Figure 3. A typical transmitted interference fringe pattern versus wave number.

process. The film thicknesses ranged from 8-20  $\mu\text{m}$  and were measured by two independent techniques, i.e. by a mechanical stylus instrument (Sloan Technology Corp. Dektak IIA) and an optical interference technique. Although the materials for the film and substrate were the same, the PVD process produced a film with a different stoichiometry and refractive index. This in turn resulted in optical interference fringes when the film-substrate composite was examined under transmission or reflection mode as a function of wavelength. The location of the maxima and minima of the fringes depends upon the optical path length ( $nd$ ), whereas the relative intensity of these fringes depends upon the difference in refractive index between the film and the substrate (Reference 6). The refractive index was determined using the optical thickness ( $nd$ ) and the physical thickness ( $d$ ) as determined by the mechanical stylus technique.

Aging effects were determined by heat treating the PVD deposited films at temperatures near but below the glass transition temperatures. A specially designed heating chamber was fabricated to accurately control the temperature and environment during the aging experiment.

### 3. RESULTS

A typical infrared transmission spectrum from a film-substrate composite is shown in Figure 3. The spectrum consists of alternate maxima and minima. They correspond to conditions of constructive and destructive interference, and depend upon the refractive indices of the substrate and film, wavelength, and the film thickness. For a transmittance curve, the conditions of minima and maxima are

### SECTION III

#### THERMAL AGING EFFECTS IN VITREOUS $\text{As}_2\text{S}_3$ FILMS

##### 1. INTRODUCTION

Vitreous  $\text{As}_2\text{S}_3$  belongs to a class of materials known as chalcogenide glasses. One of the properties of this class of materials is that it exhibits a wide spectral transparency in the infrared region of the electromagnetic spectrum. Because of the wide spectral transparency, the chalcogenide materials have found numerous applications in the areas of bulk optics, fibers, coatings, and thin films. In addition, there is a relatively large number of glass-forming chalcogenide systems with a wide range of compositional flexibility that make these vitreous chalcogenides attractive for fabrication of infrared optical devices.

The synthesis of vitreous chalcogenides, either from the liquid or vapor phase, requires special attention in order to optimize the properties. Some of the synthesis parameters of importance that have significant influence on the resulting optical properties are melting or evaporation parameters, cooling rate, and aging or annealing conditions. Although a wealth of information exists on the physical properties data of bulk vitreous chalcogenides, relatively little is known about films. Therefore, the objectives of this investigation were: (a) to develop a technique to evaluate aging in thin films, and (b) to investigate aging effects in vitreous  $\text{As}_2\text{S}_3$  films.

##### 2. EXPERIMENTAL

The  $\text{As}_2\text{S}_3$  films were vapor deposited on the Servofrax<sup>®</sup> substrate using the standard physical vapor deposition (PVD)



energy gap between the valence and conduction band. Such impurities have profound effects on the optical properties even in parts per billion (ppb) quantity. The imperfections under the discussion could be chemical impurities or physical imperfections such as dislocations or vacancies.

For bulk fluorophosphate glasses, it has been reported (Reference 4) that the impurities such as OH group and transition metal ions have a significant effect on the location of the UV absorption edge and  $dn/dT$ . The chalcogenide glasses exhibit similar characteristics. Tauc, DiSalvo, Peterson and Wood (Reference 5) have reported that the additions of Fe to amorphous  $As_2S_3$  produces optical absorption tails extending from the Urbach edge toward lower energy. They explained the effect by proposing that there are  $Fe^{2+}$  ion donor levels in  $As_2S_3$  band gap and that the optical transition originating on the  $Fe^{2+}$  ion promote an electron to the conduction band.

#### 4. CHARACTERIZATION TECHNIQUE

The characterization technique of temperature coefficient of refractive index of thin films offers another interesting problem. There are standard techniques for  $dn/dT$  determination of bulk materials, however, little is reported concerning thin films. White et al. (Reference 3) have employed an interferometric technique using a spectrometer and a temperature cell. This technique has provided useful information, nonetheless, the technique should be further modified or some other technique be developed for a precise measurement of  $dn/dT$ .

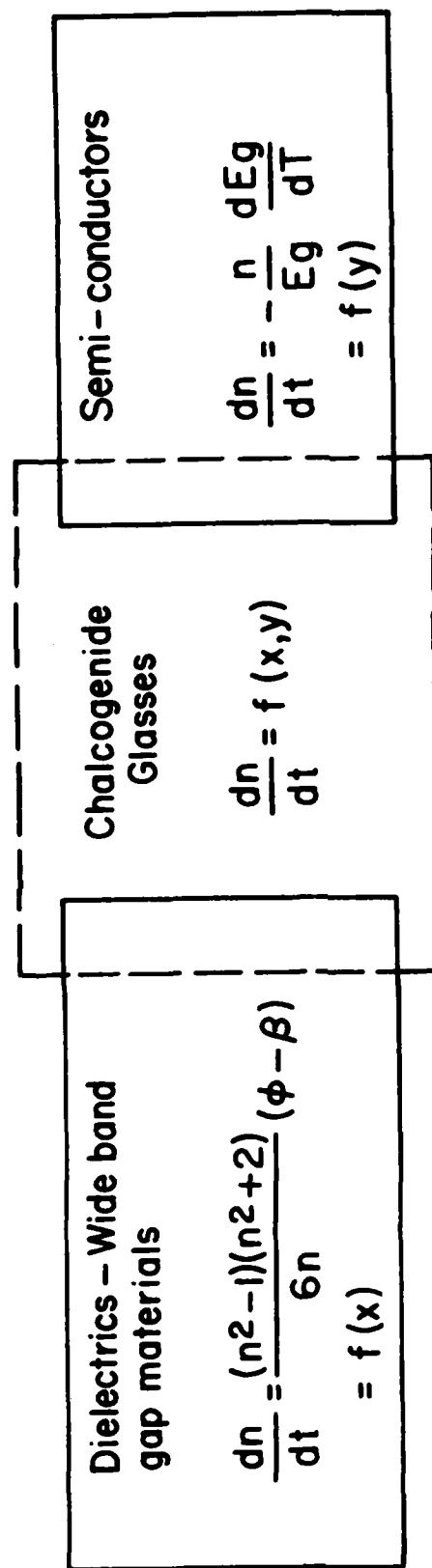


Figure 2. Temperature coefficient of refractive index of materials -- a schematic representation.

However, literature provides little information about these properties of vitreous chalcogenide type of semiconductors. Furthermore, little is known on the effects of composition on the band gap of multicomponent chalcogenide glasses. This lack of information obviously restricts our ability to design and develop vitreous chalcogenide compositions with a desired  $dn/dT$  value.

We have considered the dielectrics and semiconductors separately. However, we know that the boundary between the two materials is not well defined, and in practice there are many materials which would neither be characterized as dielectric nor semiconductors. In such a situation, probably all the parameters, i.e. the refractive index, polarizability, coefficient of thermal expansion, and the band gap would affect  $dn/dT$ . This concept is schematically illustrated in Figure 2. It is proposed that chalcogenide glasses overlap both classes of materials.

In an attempt to understand and characterize  $dn/dT$  of chalcogenide glasses, White, Phillippi and Kumar (Reference 3) have reported temperature dependence of optical path lengths ( $nd$ ) and refractive index ( $n$ ) of several compositions in the As-S and Ge-As-S systems. The  $dn/dT$  slightly varies from one composition to another; however, a definitive correlation with composition has not been established.

### 3. EFFECT OF IMPERFECTIONS

The effects of imperfections or impurities on optical properties of solids are of significant importance. We know that there are two kinds of impurities that exist in optical materials, i.e. optically active and optically inactive impurities. The optically active impurities introduce quantum levels in the

FLUORIDE  
(HBL, HBLA)<sup>2</sup>

FLUOROPHOSPHATE  
(FPI)<sup>2</sup>, (E-123, LHG10)<sup>3</sup>

PHOSPHATE  
(PIOI, Q-98, Q-100)<sup>3</sup>

SILICATE AND  
BOROSILICATE  
(ED-2, LSG-9IH, LG-600)<sup>3</sup>

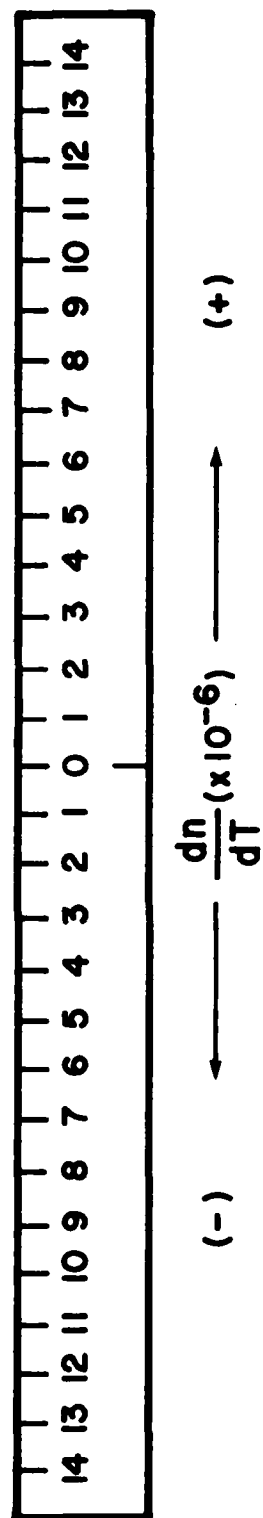


Figure 1.  $dn/dT$  range for various glass systems.

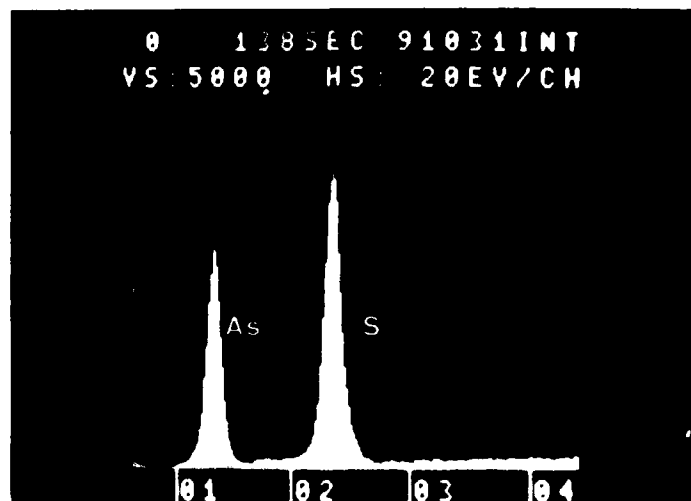


Figure 7. Typical As and S peaks observed in EDXA.

TABLE 2  
EDXA ANALYSIS OF FILM AND SUBSTRATE COMPOSITION

Deposition Rate	As	S	$S' = \frac{S}{As}$	$S'' = \frac{S}{As+S}$	$R = \frac{S_f}{S_s}$
15Å sec <sup>-1</sup>	Film	18683.52	1.4458	.5911	0.9855±.0032
	Substrate	18832.69	1.4878	.5980	
100Å sec <sup>-1</sup>	Film	16819.17	1.4532	.5923	0.9792±.0028
	Substrate	16867.19	1.5308	.6049	
210Å sec <sup>-1</sup>	Film	16844.24	1.3317	.5711	0.9684±.0037
	Substrate	11754.69	1.4375	.5897	
310Å sec <sup>-1</sup>	Film	9146.5	1.5304	.6048	0.9532±.0035
	Substrate	5919.5	1.7358	.6345	

film and substrate, respectively. The parameter R basically characterizes the sulfur concentration in the film. A value of 1 for R would represent  $\text{As}_2\text{S}_3$  stoichiometry. The R values less than 1 would represent sulfur deficiency with respect to the  $\text{As}_2\text{S}_3$  stoichiometry.

A plot of R as a function of film deposition rate is shown in Figure 8. With an increasing deposition rate, the film becomes sulfur deficient. For example, if the substrate corresponds to stoichiometric  $\text{As}_2\text{S}_3$  (As-40%, S-60), the  $15\text{\AA sec}^{-1}$  and  $210\text{\AA sec}^{-1}$  films correspond to  $\text{As}_2\text{S}_{2.905}$  (As=40.69%, S=59.31%) and  $\text{As}_2\text{S}_{2.779}$  (As=41.85%, S=58.15%) stoichiometries, respectively. The two deposition rates have led to a difference of approximately two atomic percent of sulfur concentration. The difference is further increased for the  $310\text{\AA/sec}$  deposition rate.

The effect of the deposition rate on stoichiometry would be further reflected by the physical property measurement such as refractive index and density. It is hoped to characterize these properties in the future using suitable experimental techniques.

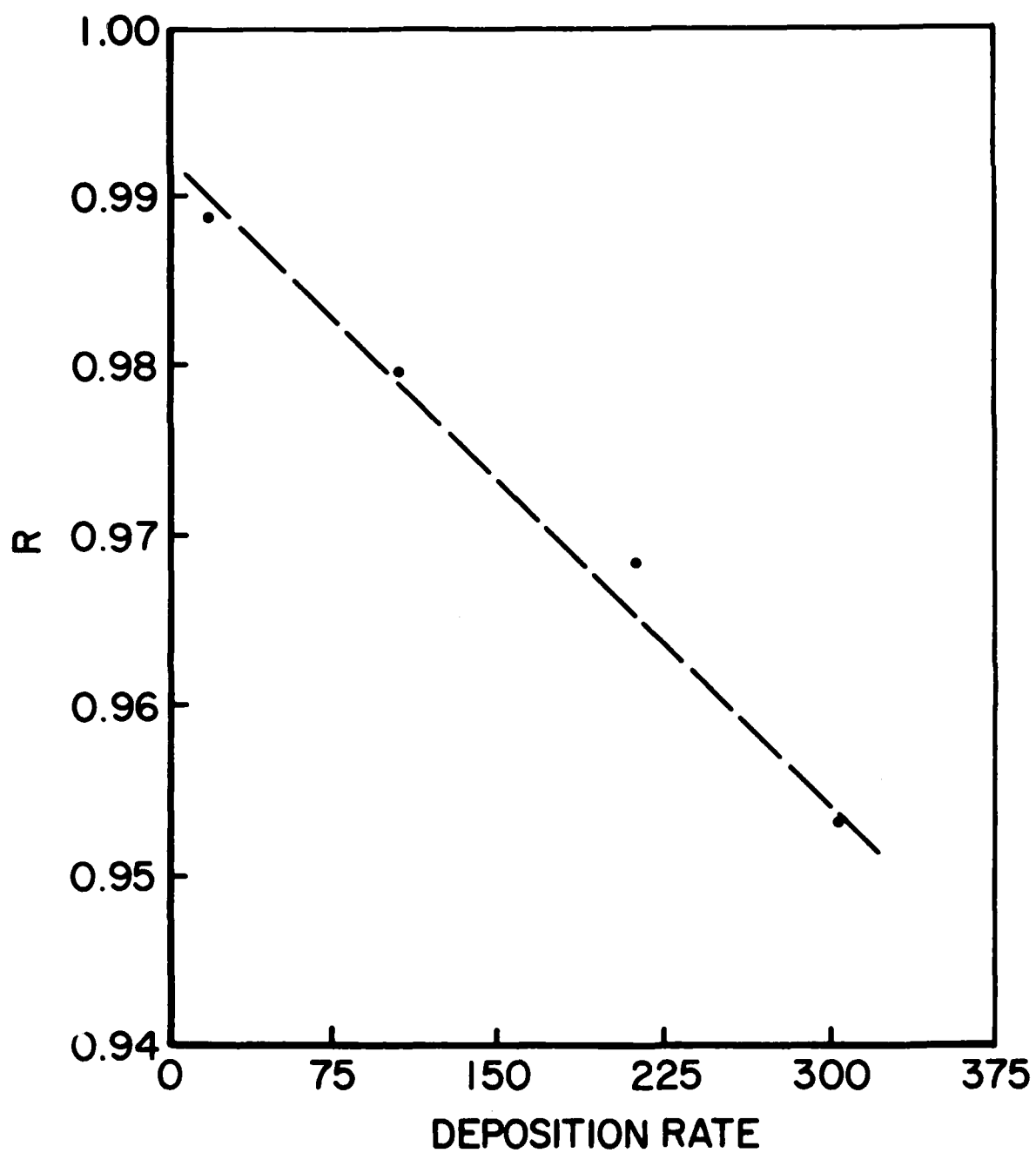


Figure 8. Plot of  $R$  as a function of film deposition rate.



## SECTION V

### SUMMARY AND CONCLUSIONS

Three different research tasks related to chalcogenide thin films have been investigated. The first two tasks deal with the thermal stability of thin films and the third task reports effects of deposition rate on stoichiometry of thin films. Specific conclusions are as follows:

1. It has been shown that a significant shift in reflection peak occurs in an optical filter due to a temperature variation. For example, if a  $\text{CO}_2$  laser is used and the temperature is raised by  $100^\circ\text{C}$ , the shift in the reflection peak is approximately  $212\text{\AA}$ .

2. The shift in reflection peak could be minimized by modifying compositions of the chalcogenide films so as to obtain zero thermal sensitivity parameter. The  $dn/dT$  is an important factor of the thermal sensitivity parameter which is not clearly understood for optical materials. It is proposed that in addition to the bulk composition, impurities play an important role in determining  $dn/dT$ .

3. An interferometric technique using an optical spectrometer has provided preliminary information on  $dn/dT$  of some chalcogenide films. For more precise measurements, either this technique has to be further modified or a new technique should be developed.

4. It has also been shown that a heat treatment (aging) of as-deposited  $\text{As}_2\text{S}_3$  films leads to a permanent increase in refractive index. The increase in refractive index is related to the heat treatment time and temperature. The increase in refractive index due to the aging amounts to about 4%.

5. There seems to be a linear relationship between the deposition rate and the stoichiometry of  $\text{As}_2\text{S}_3$  films. As the deposition rate increases, the film becomes sulfur-deficient.

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